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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Hair Setting Composition

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Abstract of the Disclosure: The hair setting compositions contain as film former a polymer based on N-vinylcaprolactam formed from

group I

- from 35 to 100 % by weight of N-vinylcaprolactam (monomer A)
- from 0 to 65 % by weight of N-vinylimidazole (monomer B) or a mixture of from 5 to 50 parts by weight of monomer B and from 10 to 60 parts by weight of N-vinylpyrrolidone (monomer C) or a mixture of from 5 to 15 parts by weight of monomer B and from 10 to 35 parts by weight of an alkyl acrylate or methacrylate having from 1 to 4 carbon atoms in the alkyl moiety (monomer D)
- from 0 to 4 % by weight of further monomer E capable of free radical copolymerization

or group II

- from 35 to 100 % by weight of monomer A
- from 0 to 65 % by weight of a mixture of from 20 to 60 parts by weight of monomer D and from 5 to 15 parts by weight of acrylic or methacrylic acid (monomer F) or of a mixture of from 15 to 50 parts by weight of monomer D and from 5 to 15 parts by weight of an alkyl acrylate or methacrylate having from 1 to 4 carbon atoms in the alkyl moiety which additionally carries unsubstituted or C₁-C₄-alkyl-substituted amino (monomer G)
- from 0 to 4 % by weight of further monomer E capable of free radical copolymerization,

any carboxyl groups of the polymer having been partly or wholly neutralized with an amine, as well as customary ingredients for this purpose.

Hair setting composition

The present invention relates to hair setting compositions which, besides the ingredients customary for this purpose, contain as film former polymers based on N-vinylcaprolactam formed from

5

group I

- from 35 to 100 % by weight of N-vinylcaprolactam (monomer A)
- 10 - from 0 to 65 % by weight of N-vinylimidazole (monomer B) or a mixture of from 5 to 50 parts by weight of monomer B and from 10 to 60 parts by weight of N-vinylpyrrolidone (monomer C) or a mixture of from 5 to 15 parts by weight of monomer B and from 10 to 35 parts by weight of an alkyl acrylate or methacrylate having from 1 to 4 carbon atoms in the alkyl moiety (monomer D)
- 15 - from 0 to 4 % by weight of further monomer E capable of free radical copolymerization

or group II

- 20 - from 35 to 100 % by weight of monomer A
- from 0 to 65 % by weight of a mixture of from 20 to 60 parts by weight of monomer D and from 5 to 15 parts by weight of acrylic or methacrylic acid (monomer F) or of a mixture of from 15 to 50 parts by weight of monomer D and from 5 to 15 parts by weight of an alkyl acrylate or methacrylate having from 1 to 4 carbon atoms in the alkyl moiety which additionally carries unsubstituted or C₁-C₄-alkyl-substituted amino (monomer G)
- 25 - from 0 to 4 % by weight of further monomer E capable of free radical copolymerization,
- 30 - from 0 to 4 % by weight of further monomer E capable of free radical copolymerization,

any carboxyl groups of the polymer having been partly or wholly neutralized with an amine.

35 Some of the polymers are novel substances. Therefore the present invention also relates to these novel substances.

DE-A-32 27 334 (1) relates to copolymers of from

20. to 75 parts by weight of a C₂-C₂₀-alkyl ester of acrylic or methacrylic acid, from 5 to 50 parts by weight of a nitrogen-containing neutral water-soluble monomer, for example N-vinylcaprolactam or N-vinylpyrrolidone, 5
from 1 to 25 parts by weight of a monomer which contains cationic groups, for example N-vinylimidazole, and from 1 to 25 parts by weight of a copolymerizable, olefinically unsaturated C₃-C₅-carboxylic acid, for example acrylic acid or methacrylic acid. The copolymers are used 10
as film formers in hair treatment compositions.

EP-B-074 191 (2) relates to a conditioning composition containing a terpolymer of a relatively large proportion of N-vinylcaprolactam, a relatively small proportion of N-vinylpyrrolidone and an ammonium deriva- 15
tive monomer, for example a dialkylaminoalkyl acrylate.

US-A-3 145 147 (3) relates to a film-forming composition comprising a copolymer of from 80 to 95 % by weight of N-vinylcaprolactam and from 5 to 20 % by weight of a polymerizable monomer, namely a vinyl ester of from 20
3 to 6 carbon atoms, an alkyl acrylate of 4 or 5 carbon atoms or an acrylamide, acrylonitrile or alkyl vinyl ether each of 3 to 4 carbon atoms.

DE-C-12 61 822 (4) describes copolymers of N-vinylcaprolactam with, for example, N-vinylimidazole or 25
with N-vinylimidazole and N-vinylpyrrolidone. The copolymers are used as agents for reducing pigment migration in the dyeing of fiber material with pigment dye liquors.

DE-A-21 12 549 (5) relates to water-soluble tetrapolymers of an N-vinyllactam, for example N-vinyl- 30
pyrrolidone or N-vinylcaprolactam, an alkyl acrylate, an alkyl methacrylate or an olefinically unsaturated carboxylic acid. The N-vinyllactam is preferably used in an amount of from 10 to 30 % by weight, based on the tetra-
polymer. The tetrapolymers are used as film formers for 35
surface coatings, textile sizes, adhesives, hair sprays and binders for sand grains and for manufacturing rocket sleeves.

Hair products are increasingly sprays containing hydrocarbons instead of halogenated hydrocarbons as propellants. The prior art copolymers used as film formers in such sprays still need to be improved in some instances in respect of their compatibility with the apolar hydrocarbons of the sprays; that is, the copolymers are still not sufficiently soluble in the hydrocarbons. Moreover, the hair setting effect of these copolymers usually still leaves something to be desired. Also, the moisture uptake of hair treated with these copolymers is still frequently too high.

It is an object of the present invention to provide film formers for hair care which should be highly compatible with apolar propellants based on hydrocarbons and should also possess a good hair setting effect and a low moisture uptake.

We have found that this object is achieved by the hair setting compositions defined at the beginning.

Group I comprises N-vinylimidazole-containing polymers, group II the N-vinylimidazole-free polymers.

For the purposes of the present invention N-vinylcaprolactam (monomer A) is N-vinyl- ϵ -caprolactam.

Suitable monomers D are in particular the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl esters of acrylic acid and of methacrylic acid. Of these, preference is given to the butyl esters, especially to the tert-butyl esters.

To achieve slight modification of the properties of the polymer, further monomers E capable of free radical copolymerization may be present in an amount of up to 4 % by weight, in particular up to 3 % by weight. Suitable monomers E are for example vinyl acetate, vinyl propionate and hydroxypropyl acetate.

Monomer F is acrylic acid or preferably methacrylic acid.

Monomer G can be in particular the methyl, ethyl, n-propyl or n-butyl esters of acrylic or methacrylic acid

which have an unsubstituted or preferably mono- or disubstituted amino group in particular at the end of the alkyl group. Particular preference is given to 2-(dialkyl-amino)ethyl methacrylates such as 2-(dimethylamino)ethyl and 2-(diethylamino)ethyl methacrylates.

Carboxyl groups present in the polymers are neutralized in whole or in part, advantageously up to from 5 to 100 %, preferably from 30 to 90 %, with an amine. The amine used is preferably

- 10 - a mono-, di- or trialkanolamine having from 2 to 5 carbon atoms in the alkanol moiety, which may be in etherified form, for example mono-, di- or triethanolamine, mono-, di- or tri-n-propanolamine, mono-, di- or triisopropanolamine, 2-amino-2-methylpropanol or di(2-methoxyethyl)amine,
- 15 - an alkanediolamine of from 2 to 5 carbon atoms, for example 2-amino-2-methyl-1,3-propanediol or 2-amino-2-ethyl-1,3-propanediol, or
- 20 - a primary, secondary or tertiary alkylamine of from 5 to 10 carbon atoms in total, for example N,N-diethylpropylamine.

Particularly good results are obtained on neutralizing with 2-amino-2-methylpropanol, triisopropanolamine and 2-amino-2-ethyl-1,3-propanediol.

- 25 Preferred polymers have the following compositions:

- from 96 to 100 % by weight of N-vinylcaprolactam (monomer A) and from 0 to 4 % by weight of monomer E;
- 30 - from 35 to 100, preferably from 50 to 90, % by weight of monomer A, from 0 to 65, preferably from 10 to 50, % by weight of N-vinylimidazole (monomer B) and from 0 to 4 % by weight of monomer E;
- 35 - from 35 to 100, preferably from 35 to 65, % by weight of monomer A, from 0 to 65, preferably from 35 to 65, % by weight of a mixture of from 5 to 50 parts by weight of monomer B and from 10 to

- 60 parts by weight of N-vinylpyrrolidone (monomer C) and also from 0 to 4 % by weight of monomer E;
- 5 - from 35 to 100, preferably from 50 to 85, % by weight of monomer A, from 0 to 65, preferably from 15 to 50, % by weight of a mixture of from 5 to 15 parts by weight of monomer B and from 10 to 35 parts by weight of monomer D and also from 0 to 4 % by weight of monomer E;
- 10 - from 35 to 100, preferably 35 to 75, % by weight of monomer A, from 0 to 65, preferably from 25 to 65, % by weight of a mixture of from 20 to 60 parts by weight of monomer D and from 5 to 15 parts by weight of monomer F, and also from 0 to 4 % by weight of monomer E;
- 15 - from 35 to 100, preferably from 45 to 80, % by weight of monomer A, from 0 to 65, preferably from 20 to 55, % by weight of a mixture of from 15 to 50 parts by weight of monomer D and from 5 to 15 parts by weight of monomer G, and also from 0 to 4 % by weight of monomer E.
- 20

Here the monomer combinations A + B + C and in particular A + B + D, A + D + F and also A + D + G, each with or without small amounts of E, represent particularly preferred embodiments.

- 25 The polymers are prepared by free radical polymerization or copolymerization of monomers A to G. The customary polymerization techniques are employed, for example, the methods of suspension, emulsion or solution polymerization.

- 30 A particularly advantageous choice is solution polymerization in an organic solvent, in general an alcohol. The polymerization is customarily carried out at from 60 to 130°C, at atmospheric pressure or under autogenous pressure.

- 35 The initiators used for the free radical polymerization reaction are the customary peroxo or azo compounds, for example dibenzoyl peroxide, tert-butyl

perpivalate, tert-butyl per-2-ethylhexanoate, di-tert-butyl peroxide, tert-butyl hydroperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane or azobisisobutyronitrile, advantageously in amounts of from 0.1 to 2 % by weight, based on the weight of the monomers.

The amounts of monomer and solvent are advantageously chosen in such a way as to produce 30-80 % strength by weight solutions of the copolymers. Any organic solvent in the solution can be removed in a conventional manner, for example by distillation, and be replaced by water if a waterborne hair setting composition is desired.

The polymers should have K values of from 10 to 60, preferably from 20 to 55. The desired K value can be set in a conventional manner through choice of the polymerization conditions, for example the polymerization time and the initiator concentration. The K values are measured by the method of Fikentscher, Cellulosechemie 13 (1932), 58-64, at 25°C in 1 % strength by weight in ethanol, and represent a measure of the molecular weight.

Such polymers customarily have glass transition temperatures of from 80 to 180, preferably from 90 to 150°C.

Some of the polymers are novel substances. For this reason the present invention also provides copolymers obtainable by free radical polymerization of

- from 35 to 95 % by weight of N-vinylcaprolactam (monomer A)
- from 5 to 65 % by weight of a mixture of from 5 to 15 parts by weight of N-vinylimidazole (monomer B) and from 10 to 35 parts by weight of monomer D
- from 0 to 4 % by weight of further monomer E capable of free radical copolymerization.

These polymers usually have K values of from 10 to 60, in particular from 20 to 55.

The present invention further provides copolymers obtainable by free radical polymerization of

- from 35 to 95 % by weight of N-vinylcaprolactam (monomer A)
- from 5 to 65 % by weight of a mixture of from 15 to 50 parts by weight of monomer D and from 5 to 15 parts by weight of monomer G
- from 0 to 4 % by weight of further monomer E capable of free radical copolymerization.

These polymers usually have K values of from 10 to 60, in particular from 20 to 55.

The hair setting compositions according to the present invention are employed for example in the form of lotions, mousses, gels and in particular sprays.

An advantageous formulation of a hair setting lotion contains:

- from 1 to 20 % by weight of the unneutralized or partially or completely neutralized polymer,
- from 0 to 99 % by weight of a customary solvent such as in particular acetone, ethanol, n-propanol, isopropanol or 1-methoxy-2-propanol or a mixture thereof, and
- from 0 to 99 % by weight of water.

A preferred hair setting lotion is predominantly aqueous and contains from 2 to 15 % by weight of polymer, from 60 to 98 % by weight of water and optionally, as remainder to 100 % by weight, one of the abovementioned solvents or mixtures thereof.

An advantageous and convenient composition for hair mousses has the following recipe:

- from 1 to 15 % by weight, preferably from 2 to 10 % by weight, of the unneutralized or partially or completely neutralized polymer,
- from 5 to 90 % by weight, preferably from 60 to 85 % by weight, of water,
- from 0 to 20 % by weight of a customary solvent such as in particular acetone, ethanol, n-propanol, isopropanol or 1-methoxy-2-propanol or a mixture thereof, and

- from 10 to 50 % by weight of a customary propellant such as propane, n-butane, isobutane, 2,2-dimethylpropane, isopentane or dimethyl ether or a mixture thereof.

5 These compositions have added to them, based on the total weight, from about 0.1 to about 1 % by weight of conventional foam formation and foam stabilization assistants.

10 Of course, the abovementioned hair setting lotions and mousses may contain further customary additives, such as scents, preservatives, etc., in the customary amounts.

As regards hair sprays, particular preference is given to those which contain the following constituents:

- 15 - from 0.1 to 20, preferably from 0.5 to 12, in particular from 2 to 10, % by weight of the unneutralized or partially or completely neutralized polymer,
- 20 - from 10 to 95, preferably from 20 to 60, in particular from 25 to 50, % by weight of a customary solvent such as, in particular, ethanol and isopropanol but also acetone, n-propanol, n-butanol, 2-methoxy-1-propanol, n-pentane, n-hexane, cyclohexane, n-heptane or dichloromethane or a mixture thereof,
- 25 - from 5 to 90, preferably from 30 to 80, in particular from 45 to 70, % by weight of a customary propellant such as propane, n-butane, isobutane, 2,2-dimethylbutane, isopentane, dimethyl ether,
- 30 fluorotrichloromethane, dichlorodifluoromethane or dichlorotetrafluoroethane or mixtures thereof. Of the propellants mentioned, in particular the hydrocarbons are used, especially propane and n-butane in a mixture in a weight ratio of for example from
- 35 40 : 60 or 25 : 75 or n-butane alone. If desired, one or more of the chlorofluorocarbons are included in the propellant mixture, but only in small

amounts, say up to 20 % by weight, based on the propellant mixture.

Additionally these sprays may contain small amounts of perfume oils, for example from 0.1 to 5.0 % by weight.

The customary constituents and compositions of other hair setting products are known to those skilled in the art and consequently need not be explained here at length.

The polymers of the hair setting compositions according to the present invention are highly compatible with the apolar propellants employed in sprays, in particular with hydrocarbons such as propane or n-butane or a mixture thereof. In general, they produce compatibility values within the range from 50 to 85, in particular from 70 to 85, % by weight coupled with a remarkably good hair setting effect, as evidenced by the high curl retention values, which in their case is normally within the range from 70 to 95 %, in particular from 85 to 95 %. The moisture uptake of the treated hair is low, within the range from 3 to 18, in particular from 3 to 10, % by weight, as a result of which the hair is kept in place for longer and is less sticky.

Furthermore, the hair setting compositions according to the present invention are in fact notable for not causing the hair to stick together to any practical extent; it remains readily combable. The treated hair has a natural appearance. The stiffening effect achieved on the hair with compositions according to the present invention is generally good.

EXAMPLES

The known polymers used in the hair setting compositions according to the present invention were prepared by the usual methods of solution polymerization. In what follows, the preparation of the polymer of Example 10 will be described and should be taken as representative of all the other methods of preparation.

Preparation of a polymer of 60 % by weight of N-vinylcaprolactam, 10 % by weight of N-vinylimidazole and 30 % by weight of tert-butyl acrylate.

5 A solution of 30 g of N-vinylcaprolactam, 5 g of N-vinylimidazole, 15 g of tert-butyl acrylate and 0.53 g of tert-butyl perpivalate (75 % strength by weight) in 275 g of ethanol was heated to 75°C. Once the polymerization has started, as evidenced by an increase in the viscosity, a mixture of 270 g of N-vinylcaprolactam, 45 g of N-vinylimidazole, 135 g of tert-butyl acrylate and 100 g of ethanol and a solution of 2.4 g of tert-butyl perpivalate (75 % strength by weight) and 60 g of ethanol were added simultaneously in the course of 3 hours while the temperature was maintained at 77-80°C with slow boiling. Thereafter a solution of 2.4 g of tert-butyl perpivalate (75 % strength by weight) in 60 g of ethanol was added dropwise at the same temperature in the course of a further 3 hours.

20 Then 3.0 g of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane were added all at once. The reaction vessel was sealed pressure-tight, heated to 130°C and maintained at that temperature for 3 hours.

Properties of the polymers

25 Tables 1 to 6 below show the composition, K value, hydrocarbon compatibility, hair setting effect and moisture uptake of the polymers used in the compositions according to the present invention.

The K value was measured at 25°C on a 1.0 % strength by weight solution in ethanol.

30 The hydrocarbon compatibility, determined with a 25 : 75 w/w mixture of propane and n-butane, indicates the maximum weight percentage of this propellant gas mixture which may be present in a spray formulation which, besides ethanol as solvent, contains 3 % by weight of the copolymer, whose carboxyl groups, if it has any, are 75 % neutralized with 2-amino-2-methylpropanol, without causing cloudiness at 0°C.

5 The hair setting effect is measured in terms of
curl retention. Curl retention is measured in an in vitro
test on curls formed from approximately 15 cm long
strands of hair by a customary shampoo-and-set treatment
and sprayed with the particular spray formulation from a
distance of 10 cm for 4 seconds. After the suspended
curls have been conditioned in a conditioning cabinet at
25°C and 90 % relative humidity for 5 hours, the relative
opening-out or uncurling of the curls is determined
10 relative to their original shape. A high value denotes
high shape retention; that is, a value of 100 % would
denote that the original shape was completely retained.

The curl retention values for the polymers
designated in Tables 1 to 6 were determined in each case
15 with the following standard spray formulation:

6.3 % by weight of polymer which, if any carboxyl
groups were present, has been 75 %
neutralized with 2-amino-2-methyl-
propanol,
20 33.7 % by weight of ethanol and
60.0 % by weight 25:75 propane/n-butane.

The moisture uptake of the polymer-treated hair
from the surrounding air was measured after 7 days at
75 % relative humidity.

TABLE 1

Polymers of monomers A and E

Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]
5					
10					
	[% by weight]				
15	1 100 of N-vinyl-caprolactam	32.1	75	82	9.3
	2 97 of N-vinyl-caprolactam 3 of vinyl acetate	20.4	74	83	9.4
20	For comparison:				
	A 80 of N-vinyl-caprolactam 20 of vinyl acetate	29.8	72	83	9.7
25					

Example A was prepared according to reference (3); the aqueous solution of A, unlike those of Examples 1 and 2, was not colorless and the hair treated with A was gray and scaly.

TABLE 2

Polymers of monomers A and B

Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]	
5						
10						
15	3	40 of N-vinyl-caprolactam 60 of N-vinyl-imidazole	45.0	50	83	18.0
20	4	50 of N-vinyl-caprolactam 50 of N-vinyl-imidazole	43.9	56	85	14.7
25	5	60 of N-vinyl-caprolactam 40 of N-vinyl-imidazole	42.8	57	87	16.6
	6	70 of N-vinyl-caprolactam 30 of N-vinyl-imidazole	43.2	61	88	15.4
30	7	80 of N-vinyl-caprolactam 20 of N-vinyl-imidazole	43.6	65	91	13.7

TABLE 3

Polymers of monomers A, B and C

Ex-ample	Composition [% by weight]	K value	Hydro-carbon compat- ibility with 25:75 propane/- n-butane [% by weight]	Curl reten- tion [%]	Mois- ture up- take [% by weight]
5					
10					
15	8 35 of N-vinyl- caprolactam 50 of N-vinyl- imidazole 15 of N-vinyl- pyrrolidone	46.1	52	79	18.0
20	9 60 of N-vinyl- caprolactam 30 of N-vinyl- imidazole 10 of N-vinyl- pyrrolidone	40.4	63	93	14.1
25					

TABLE 4

Polymers of monomers A, B and D

	Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]
5						
10						
		[% by weight]				
15	10	60 of N-vinyl-caprolactam 10 of N-vinyl-imidazole 30 of tert-butyl acrylate	27.6	76	89	5.8
20	11	75 of N-vinyl-caprolactam 5 of N-vinyl-imidazole 20 of tert-butyl acrylate	29.3	75	87	6.4
25						
	12	75 of N-vinyl-caprolactam 5 of N-vinyl-imidazole 20 of methyl acrylate	27.8	60	86	8.0
30						
	13	75 of N-vinyl-caprolactam 5 of N-vinyl-imidazole 20 of ethyl acrylate	53.0	74	84	7.1
35						

TABLE 5

Polymers of monomers A, D and F

Ex- ample	Composition [% by weight]	K value	Hydro- carbon compat- ibility with 25:75 propane/- n-butane [% by weight]	Curl reten- tion [%]	Mois- ture up- take [% by weight]
5					
10					
15	14 40 of N-vinyl- caprolactam 55 of tert-butyl acrylate 5 of methacrylic acid	24.2	77	90	4.0
20	15 40 of N-vinyl- caprolactam 50 of tert-butyl acrylate 10 of methacrylic acid	27.6	71	90	5.7
25	16 40 of N-vinyl- caprolactam 45 of tert-butyl acrylate 15 of methacrylic acid	26.3	61	89	6.5
30	17 50 of N-vinyl- caprolactam 45 of tert-butyl acrylate 5 of methacrylic acid	25.1	75	90	5.4
35					
40	18 60 of N-vinyl- caprolactam 35 of tert-butyl acrylate 5 of methacrylic acid	26.9	75	90	7.1

TABLE 5 (continued)

Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]
5					
10					
	[% by weight]				
15	19 70 of N-vinyl-caprolactam	28.7	75	88	7.3
	25 of tert-butyl acrylate				
	5 of methacrylic acid				
20	20 70 of N-vinyl-caprolactam	29.4	74	82	9.3
	25 of n-butyl acrylate				
	5 of methacrylic acid				
25	21 70 of N-vinyl-caprolactam	29.3	66	70	10.0
	20 of n-butyl acrylate				
30	10 of methacrylic acid				
	22 75 of N-vinyl-caprolactam	33.3	75	84	6.3
	20 of n-butyl methacrylate				
35	5 of methacrylic acid				
	23 70 of N-vinyl-caprolactam	27.6	64	72	7.4
	25 of ethyl acrylate				
40	5 of methacrylic acid				

TABLE 5 (continued)

Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]
5					
10	[% by weight]				
For comparison:					
15	B 20 of N-vinyl-pyrrolidone 9 of N-vinyl-imidazole 64 of tert-butyl acrylate	17.0	65	22	7.4
20	7 of acrylic acid				

Example B corresponds to Example 5 of reference (1).

TABLE 6

25 Polymers of monomers A, D and G

Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]
30					
35	[% by weight]				
40	24 45 of N-vinyl-caprolactam 45 of tert-butyl acrylate 10 of DMAEMA	24.3	80	95	3.3
45	25 55 of N-vinyl-caprolactam 40 of tert-butyl acrylate 5 of DMAEMA	24.4	80	96	3.8

TABLE 6 (continued)

Ex-ample	Composition	K value	Hydro-carbon compat-ibility with 25:75 propane/-n-butane [% by weight]	Curl reten-tion [%]	Mois-ture up-take [% by weight]
5					
10	[% by weight]				
26	60 of N-vinyl-caprolactam	25.6	75	90	7.1
15	35 of tert-butyl acrylate				
	5 of DMAEMA				
27	65 of N-vinyl-caprolactam	27.3	78	96	5.3
20	30 of tert-butyl acrylate				
	5 of DMAEMA				
28	75 of N-vinyl-caprolactam	27.2	76	86	6.9
25	20 of tert-butyl acrylate				
	5 of DMAEMA				
29	65 of N-vinyl-caprolactam	39.8	75	93	6.3
30	30 of n-butyl methacrylate				
	5 of DMAEMA				
30	75 of N-vinyl-caprolactam	33.3	84	75	6.7
35	20 of n-butyl methacrylate				
	5 of DMAEMA				
	For comparison:				
C	47.5 of N-vinyl-caprolactam	43.9	80	70	3.9
40	47.5 of N-vinyl-pyrrolidone				
	5 of DMAEMA				
45	DMAEMA: 2-(dimethylamino)ethyl methacrylate				

Example C corresponds to the third example of Table III of reference (2), where, however, the curl retention was found to be 89-90 % under significantly gentler conditions (45 minutes instead of 5 hours).

5 Formulation examples for hair setting compositions

EXAMPLE 31

Hair setting lotion with alcohol

- 10.0 % by weight of N-vinylcaprolactam polymer of Example 1
- 10 5.0 % by weight of ethanol
- 85.0 % by weight of water

The solution obtained was slightly opalescent.

EXAMPLE 32

Hair setting lotion without alcohol

- 15 10.3 % by weight of N-vinylcaprolactam/tert-butyl acrylate/methacrylic acid polymer of Example 19, 100 % neutralized with 2-amino-2-methylpropanol
- 0.2 % by weight of customary preservative
- 20 89.5 % by weight of water

The solution obtained was clear.

EXAMPLE 33

Hair mousse with setting ingredient

- 25 6.0 % by weight of N-vinylcaprolactam polymer of Example 9
- 0.1 % by weight of addition product of cetyl-stearyl alcohol with 25 mol of ethylene oxide
- 0.3 % by weight of cetyldimethyl-2-hydroxyethylammonium dihydrogenphosphate
- 30 0.4 % by weight of customary perfume
- 0.2 % by weight of customary preservative
- 83.0 % by weight of water
- 10.0 % by weight of 25:75 propane/n-butane

- 35 The result was an appealing, firm and somewhat creamy mousse.

EXAMPLE 34

Hair mousse with conditioner and setting ingredient

- 4.0 % by weight of N-vinylcaprolactam polymer of Example 9
- 5 5.0 % by weight of vinylpyrrolidone/vinylimidazolium methohloride copolymer
- 0.5 % by weight of cetyldimethyl-2-hydroxyethylammonium dihydrogenphosphate
- 0.4 % by weight of customary perfume
- 10 0.2 % by weight of customary preservative
- 79.9 % by weight of water
- 10.0 % by weight of 25:75 propane/n-butane

The result obtained was a firm, dry mousse.

EXAMPLE 35

15 Hair gel

- 6.0 % by weight of N-vinylcaprolactam polymer of Example 9
- 0.6 % by weight of polyacrylic acid
- 11.0 % by weight of N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine
- 20 20.0 % by weight of ethanol
- 62.4 % by weight of water

The result obtained was an opalescent gel having a good setting effect.

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EXAMPLE 36

Hair spray formulation (standard)

- 6.3 % by weight of N-vinylcaprolactam/tert-butyl acrylate/2-(dimethylamino)ethyl methacrylate polymer of Example 25
- 30 33.7 % by weight of ethanol
- 60.0 % by weight of 25:75 propane/n-butane

The cloud point was below -35°C. A predominant portion of the ethanol was replaceable by n-pentane or n-hexane without adverse effect on the hair setting action.

Hair spray formulation

35.9 % by weight of ethanol

60.0 % by weight of n-butane

The cloud point was below -35°C .

Hair spray formulation

51.5 % by weight of ethanol

40.0 % by weight of n-butane

The cloud point was below -35°C .

Hair spray formulation

38.0 % by weight of ethanol

25 50.0 % by weight of n-butane

The cloud point was below -35°C .

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A hair setting composition, containing as film former a polymer based on N-vinylcaprolactam formed from group I

- from 35 to 100 % by weight of N-vinylcaprolactam (monomer A)
- from 0 to 65 % by weight of N-vinylimidazole (monomer B) or a mixture of from 5 to 50 parts by weight of monomer B and from 10 to 60 parts by weight of N-vinylpyrrolidone (monomer C) or a mixture of from 5 to 15 parts by weight of monomer B and from 10 to 35 parts by weight of an alkyl acrylate or methacrylate having from 1 to 4 carbon atoms in the alkyl moiety (monomer D)
- from 0 to 4 % by weight of further monomer E capable of free radical copolymerization

or group II

- from 35 to 100 % by weight of monomer A
- from 0 to 65 % by weight of a mixture of from 20 to 60 parts by weight of monomer D and from 5 to 15 parts by weight of acrylic or methacrylic acid (monomer F) or of a mixture of from 15 to 50 parts by weight of monomer D and from 5 to 15 parts by weight of an alkyl acrylate or methacrylate having from 1 to 4 carbon atoms in the alkyl moiety which additionally carries unsubstituted or C₁-C₄-alkyl-substituted amino (monomer G)
- from 0 to 4 % by weight of further monomer E capable of free radical copolymerization,

any carboxyl groups of the polymer having been partly or wholly neutralized with an amine, as well as customary ingredients for this purpose.

2. A hair setting composition as claimed in claim 1, in which the polymer is formed from

- 96 - 100 % by weight of N-vinylcaprolactam (monomer A) and
- 0 - 4 % by weight of further monomer E capable of free radical copolymerization.

3. A hair setting composition as claimed in claim 1, in which the polymer is formed from
- 35 - 100 % by weight of N-vinylcaprolactam (monomer A),
 - 0 - 65 % by weight of N-vinylimidazole (monomer B)
 - 0 - 4 % by weight of further monomer E capable of free radical copolymerization.
4. A hair setting composition as claimed in claim 1, in which the polymer is formed from
- 35 - 100 % by weight of N-vinylcaprolactam (monomer A)
 - 0 - 65 % by weight of a mixture of 5 - 50 parts by weight of N-vinylimidazole (monomer B) and 10 - 60 parts by weight of N-vinylpyrrolidone (monomer C)
 - 0 - 4 % by weight of further monomer E capable of free radical copolymerization.
5. A hair setting composition as claimed in claim 1, in which the polymer is formed from
- 35 - 100 % by weight of N-vinylcaprolactam (monomer A)
 - 0 - 65 % by weight of a mixture of 5 - 15 parts by weight of N-vinylimidazole (monomer B) and 10 - 35 parts by weight of monomer D
 - 0 - 4 % by weight of further monomer E capable of free radical copolymerization.
6. A hair setting composition as claimed in claim 1, in which the polymer is formed from
- 35 - 100 % by weight of N-vinylcaprolactam (monomer A)
 - 0 - 65 % by weight of a mixture of 20 - 60 parts by weight of monomer D and 5 - 15 parts by weight of acrylic acid or methacrylic acid (monomer F)
 - 0 to 4 % by weight of further monomer E capable of free radical copolymerization.
7. A hair setting composition as claimed in claim 1, in which the polymer is formed from
- 35 - 100 % by weight of N-vinylcaprolactam (monomer A)

- 0 - 65 % by weight of a mixture of 15 - 50 parts by weight of monomer D and 5 - 15 parts by weight of monomer G
 - 0 - 4 % by weight of further monomer E capable of free radical copolymerization.
8. A copolymer as set forth in claim 5, obtainable by free radical polymerization of
- from 35 to 95 % by weight of N-vinylcaprolactam (monomer A)
 - from 5 to 65 % by weight of a mixture of from 5 to 15 parts by weight of N-vinylimidazole (monomer B) and from 10 to 35 parts by weight of monomer D
 - from 0 to 4 % by weight of further monomer E capable of free radical copolymerization.
9. A copolymer as set forth in claim 7, obtainable by free radical polymerization of
- from 35 to 95 % by weight of N-vinylcaprolactam (monomer A)
 - from 5 to 65 % by weight of a mixture of from 15 to 50 parts by weight of monomer D and from 5 to 15 parts by weight of monomer G
 - from 0 to 4 % by weight of further monomer E capable of free radical copolymerization.
10. A method for setting hair, which comprises using a copolymer as set forth in claim 1 as film former.
11. A hair setting composition in the form of a spray, containing from 0.1 to 20 % by weight of a polymer as set forth in claim 1, as well as customary solvents and propellants.